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α-Glucosidase inhibition properties of novel azaphthalocyanines containing vanillin

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Vanillin substituted novel zinc(II) azaphthalocyanines (ZnAzaPcs) have been synthesized and investigated for their α-glucosidase inhibition properties. The new compounds (**1**, **2**, **1a** and **2a**) have been characterised using a combination of FT-IR, ^{1}H and ^{13}C NMR, UV-Vis, MS and elemental analysis. The crystal structures of starting pyrazine compounds **1** and **2** have also been determined by the single crystal diffraction technique. All newly synthesized compounds have been evaluated for their *in vitro* inhibitory activity against α-glucosidase and all of them have more inhibitory effect when compared to acarbose as reference compound. Especially, compound **2** shows the most significant α-glucosidase inhibition. IC_{50} values of compound **2** and acarbose, which is known as α-glucosidase inhibitor used as anti-diabetic drug, have been found to be 6.01±0.16 and 9.52±0.23 μg/mL, respectively.

Keywords: Azaphthalocyanine, Vanillin, α-Glucosidase inhibition

Control of postprandial hyperglycemia is an essential component of diabetes treatment. Alpha glucosidase inhibitors are a class of oral antidiabetic drugs that primarily act on postprandial hyperglycemia. They regulate the availability of glucose for intestinal absorption by modification of carbohydrate digestion. Three alpha glucosidase inhibitors are in therapeutic use: acarbose, miglitol, and voglibose. Control of HbA1c is equipotent to other oral antidiabetics. Alpha glucosidase inhibitors exert beneficial effects on major components of the metabolic syndrome, microbiota, and cardiovascular risk factors. Acarbose has evidence-based effects of prevention of type 2 diabetes and cardiovascular risk in patients with impaired glucose tolerance.

Azaphthalocyanines (AzaPcs) are aza-analogs of phthalocyanines (Pcs), in which some of the C atoms in the Pc macrocycle are replaced with N atoms[5]. These macrocycles have attracted considerable attention due to their promising photosensitive[16], fluorescent[14], non-linear optical[15] and oxidative properties[12]. Eight additional N atoms on the periphery of AzaPcs increase the polarities of these macrocycles, and substituents may be used to modify solubility, UV-Vis absorption *i.e.* shifts of Q-bands, and acid-base properties[7].

Vanillin is phenolic compound that widely distribute in various plants and also be found in common foods and plant origin which definitely have positive effect on human health because of their anti–allergic, anti–artherogenic, anti–inflammatory, antioxidant, antimutagens and antimicrobial activity[2].

Studies on enzyme inhibition of AzaPcs have been scarcely reported, however some Pc and AzaPc compounds was previously reported as enzyme inhibitory by our group[3,4].

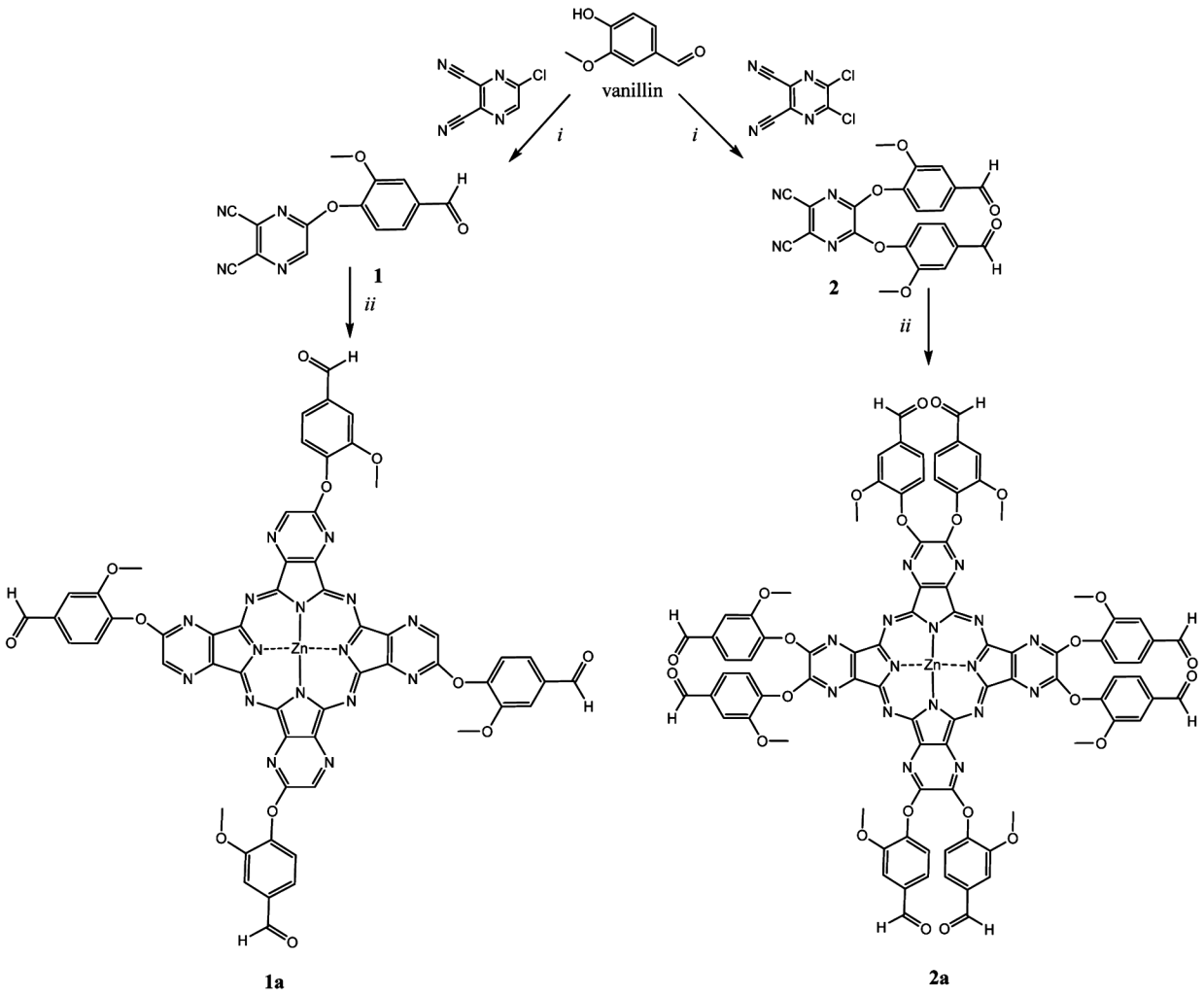
The purposes of this research (i) synthesis and characterize vanillin substituted AzaPc (ii) to investigation the spectroscopic and α-glucosidase inhibitory properties of the novel AzaPc.

Results and Discussion

Synthesis and Characterization

5-Chloropyrazine-2,3-dicarbonitrile and 5,6-dichloropyrazine-2,3-dicarbonitrile were prepared according to literature procedures[8,9]. The synthetic route of the novel azaphthalocyanines (M: Zn) containing vanillin can be seen in Scheme 1.

The novel pyrazine dinitrile derivatives **1** and **2** were prepared by treatment of 5-chloropyrazine-2,3-dicarbonitrile and 5,6-dichloropyrazine-2,3-dicarbonitrile with vanillin, respectively. After, azaphthalocyanines were obtained by heating pyrazine dinitrile compounds **1** and **2** with $Zn(CH_3COO)_2$ salt for 20 min. Characterisation of the whole compounds has been completed by FT-IR,



Scheme 1 — Synthetic route of compounds **1**, **2** and azaphthalocyanines **1a** and **2a**: (i) Triethylamine/THF, 65°C, 24 h. (ii) Metal salt, 250°C, 20 min.

x-ray diffraction analysis, UV-Vis spectroscopy, ^{1}H NMR, ^{13}C NMR, elemental analysis and MS. Elemental analysis results of the compounds **1, 2, 1a** and **2a** showed well overlap with the calculated values.

FT-IR spectra of compounds **1** and **2** show characteristic C≡N peaks at 2243 and 2238 cm^{-1}, respectively.

In the ^{1}H NMR spectrum of compound **1**, aldehyde group proton was observed at δ 10.004 as a singlet, aromatic peaks at δ 9.109 as a singlet at δ 7.704-7.521 as two doublets and one singlet, methoxy protons at δ 3.816 as a singlet.

In the ^{1}H NMR spectrum of compound **2,** aldehyde proton was appeared at δ 10.023, aromatic peaks at δ 7,743-7,739 and 7,621-7,601 as two doublets and at δ 7.701-7.681 as a doublet-doublet, and methoxy (-OCH_3) protons at δ 3,879 as a singlet.

The ^{13}C NMR spectra of compounds **1** and **2** compatible to suggested structures. The ^{13}C NMR spectrum of compound **1** indicated the existence of nitrile carbon atoms at δ 113.88 and 113.27 and the peak for the C=O carbon at at δ 192.39.

The ^{13}C NMR spectrum of compound **2** showed the presence of nitrile carbon atoms at δ 113.88 and C=O carbon at δ 192.41.

FT-IR spectra of compound **1a** and **2a** were clearly indicated that phthalocyanine formation the disappearing characteristic C≡N peaks at 2243 and 2238 cm^{-1}.

In the ^{1}H NMR spectrum of compound **1a** aldehyde proton was observed at δ 10.20, aromatic peaks at δ 9,36-7,53 as a multiplet and methoxy protons at δ 3.99-3.81.

In the ^{1}H NMR spectrum of compound **2a** aldehyde proton was observed at 10.02 as a singlet, aromatic

peaks at 7.73-7.60 as a multiplet and methoxy protons at δ 3.87 as a singlet.

High resolution mass spectra of compounds **1a** and **2a** provided definitive proof of their structure. Ionisation took place in DMSO solution. Molecular ion peaks of compounds **1a** and **2a** were detected. MS spectrum measurements confirmed unambiguously the molecular mass of compounds **1a** (ESI-TOF m/z =1186.58 M^+), and **2a** (MALDI-TOF m/z = 1787.5 M+1).

The new azaphthalocyanines (**1a** and **2a**) showed two strong absorption regions in their UV/Vis spectrum in solutions, one in the UV region between 355 and 338 nm (B band) and the other in the visible region between 635 and 631 nm (Q band) in DMSO, respectively. The UV/Vis spectra of the newly synthesised azaphthalocyanines **1a** and **2a** are shown in Fig. 1.

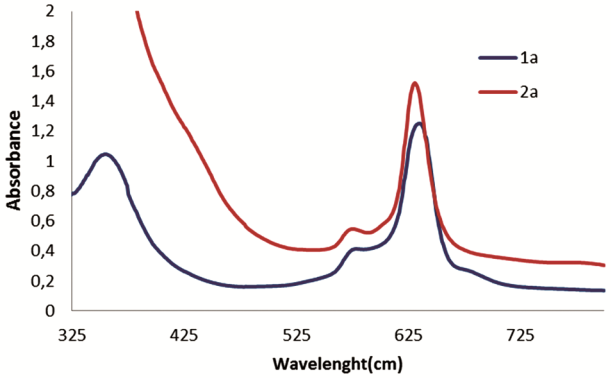


Fig. 1 — UV-Vis spectra of azaphthalocyanines **1a** and **2a** in DMSO

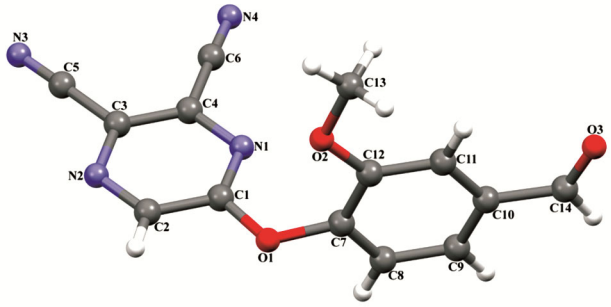


Fig. 2 — The structure of compound **1** exhibition the atom numbering scheme

Crystallographic analysis of compounds 1 and 2

The molecular structure of **1** with the atom labeling is shown in Fig. 2. The nitriles are equivalent and typical of N≡C triple bonds [N3-C5=1.138 (2) Å and N4-C6=1.136 (3) Å] (Table 1). The dihedral angle between pyrazine and phenyl rings is 89.33(6)°.

The pyrazine ring plane is approximately planar, with maximum deviation from the least-squares plane being 0.0069(12) Å for atom C1. The molecules of **1** are connected by C-H···O hydrogen bonds and C-H···π interactions (Table 2). Atom C13 atom acts as hydrogen-bond donor, *via* atom H13A, to atom O2 in the molecule at (−x+1, −y+2, −z+1), forming a centrosymmetric $R_2^2(6)$ ring centered at (1/2, 1, 1/2). Similarly, atom C13 in the molecule at (x, y, z) acts as hydrogen-bond donors to the C7∼C12 phenyl ring in the molecule at (1-x, 1-y, 1-z), so forming a centrosymmetric $R_2^2(10)$ ring centered at (1/2, 1/2, 1/2). The combination of the hydrogen bonds generates a chain of edge-fused $R_2^2(6)$ and $R_2^2(10)$ rings running parallel to the [010] direction (Fig. 3).

The molecular structure of **2** with the atom labeling is shown in Fig. 4. The N≡C bond distances are 1.132(7) Å and 1.144(9) Å, respectively. The pyrazine ring make dihedral angles of 80.45 (16) and 89.25 (16) with the two phenyl rings. The dihedral angle of the phenyl rings is 8.99(39)°. The pyrazine ring plane is approximately planar, with maximum deviation from the least-squares plane being 0.0058(33) Å for atom C4. The molecules of **2** are connected by C-H···O and C-H···N hydrogen bonds (Table 2). Atom C11 atom acts as hydrogen-bond donor, *via* atom H11, to atom O3 in the molecule at (-x, -y+1,

Table 1 — Selected bond distances and angles for **1-2** (Å, º)

Compd **1**	C5-N3	1.138 (2)	C6-N4	1.136 (3)
	C1-O1-C7	118.45 (14)		
Compd **2**	C5-N3	1.132 (7)	C6-N4	1.144 (9)
	C1-O1-C7	117.5 (4)	C2-O4-C15	116.3 (4)

Table 2 — Hydrogen bonds parameters for **1-2** (Å, °)

	D-H···A	D-H	H···A	D···A	D-H···A
Compd **1**	C13-H13A···O2^{i}	0.96	2.53	3.395 (3)	149
	C13-H13B···Cg(2)^{ii}	0.96	2.96	3.775	143
Compd **2**	C11-H11···O3^{i}	0.95	2.60	3.545 (9)	179
	C16-H16···N3^{ii}	0.95	2.60	3.473 (8)	154

Symmetry codes: (i) −x+1, −y+2, −z+1; (ii) 1-x, 1-y, 1-z; Cg(2)= C7-C12 for 1.
Symmetry codes: (i) −x, −y+1, −z; (ii) x, −y+1/2, z−1/2 for **2**.

-z), forming a centrosymmetric $R_2^2(10)$ ring centered at (0, 0, 1/2). Atom C16 atom acts as hydrogen-bond donor, *via* atom H16, to atom N3 in the molecule at (x, -y+1/2, z-1/2), forming a C(9) chain running which is parallel to the [001] direction (Fig. 5).

α-Glucosidase inhibition assay analysis

The all synthesized compounds were evaluated for their *in vitro* inhibitory activity against α-glucosidase and compounds **1** and **2** showed good inhibition at various concentrations. No significant inhibitory effect was detected for azaphthalocyanine compounds. Among the tested compounds, compound **2** showed the most significant α-glucosidase inhibition. Also, the compounds had more inhibitory effect when compared to acarbose as reference compound. IC_{50} values of Compounds **1**, **2** and acarbose known as α-glucosidase inhibitor used as anti-diabetic drug, were found 13.46±0.39, 6.01±0.16 and 9.52±0.23 µg/mL, respectively (Table 3, Fig. 6). These compounds have a considerable inhibition potential.

Experimental Section

5-Chloropyrazine-2,3-dicarbonitrile and 5,6-dichloropyrazine-2,3-dicarbonitrile were prepared according to literature[8,9]. Vanillin (Sigma, UK), *p*-Nitrophenol palmitate (*p*NPP) were obtained from Sigma, UK. Spectroscopic analyses were accomplished by UV-Vis spectra (Perkin-Elmer) UV-Vis spectrophotometer, FT-IR spectra by Perkin-Elmer Spectrum 100. ^{1}H and ^{13}C NMR (Agilent 400 FT-NMR), elemental analyses at RTEÜ Research Centre (Rize, Turkey), mass analyses (Agilent LC/MS-TOF) at GRÜMLAB Research Centre (Giresun, Turkey).

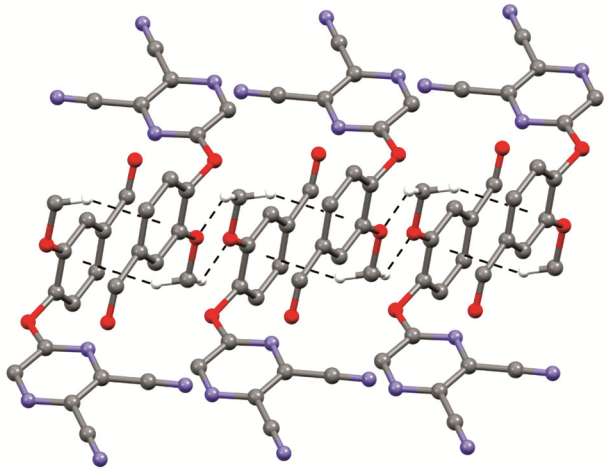


Fig. 3 — Part of the crystal structure of **1**, showing the formation of edge-fused $R_2^2(6)$ and $R_2^2(10)$ rings. H atoms not involved in these interactions have been omitted for clarity.

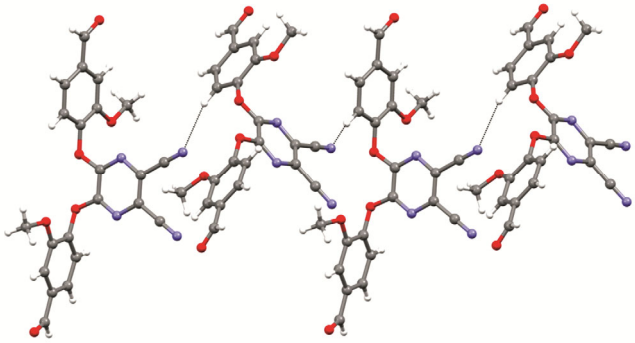


Fig. 5 — Crystal structure of **3**, showing the formation of a chain along [001] generated by C-H···N hydrogen bonds

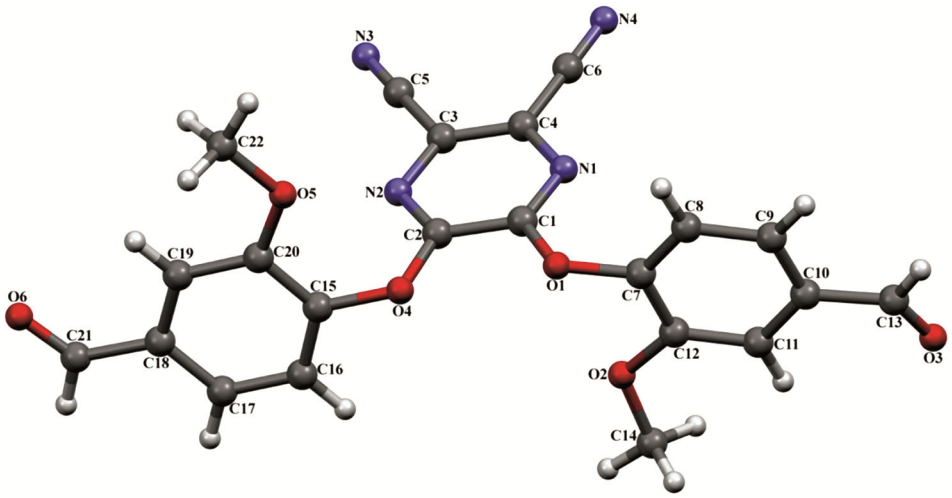


Fig. 4 — The structure of compound **2** exhibition the atom numbering scheme

Table 3 — Residual α-Glucosidase activity (at final concentration of 100 µg/mL) and IC_{50} values of the selected synthesized compounds. Acarbose was used as positive control.

Compd	α-Glucosidase	
	% Remaining Activity	IC_{50} (µg/mL)
T+	100	–
1 (100 µg/mL)	5.13±1.09	13.46±0.39
1a (100 µg/mL)	97.64±0.97	nd
2 (100 µg/mL)	1.40±0.69	6.01±0.16
2a (100 µg/mL)	98.27±1.56	nd
Acarbose (100 µg/mL)	2.06±0.46	9.52±0.23

T+: α-Glucosidase without inhibitor (control), Acarbose; positive control, nd: **not detected/observed**

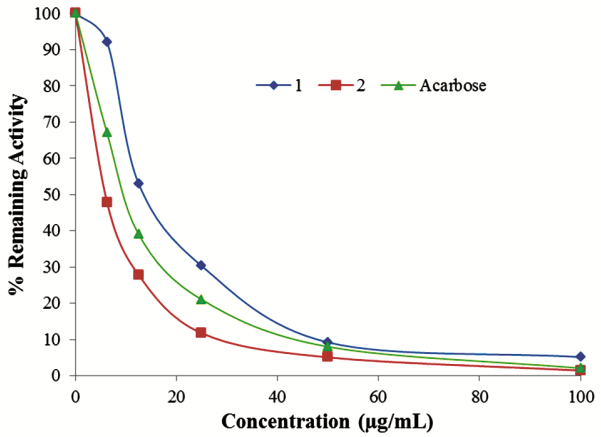


Fig. 6 — IC_{50} values of the selected synthesized compounds and acarbose as standard inhibitor against α-Glucosidase from *Saccharomyces cerevisiae*

5-(4-Formyl-2-methoxyphenoxy)pyrazine-2,3-dicarbonitrile, 1

5-Chloropyrazine-2,3-dicarbonitrile (0.3 g, 1.8 mmol) and 4-hydroxy-3-methoxybenzaldehyde (0.27 g, 1.8 mmol) were stirred in 15 mL tetrahydrofuran (THF) at 65°C. Then triethylamine (0.25 mL, 1.8 mmol) was added to the mixture and stirred at 65°C for 24 h. After the mixture was evaporated to dryness the remaining residue was dissolved in ethanol and then precipitated by addition of water. The light yellow precipitate was collected by filtration. The product was purified by crystallisation from dry amyl alcohol.

The yield of white crystals 93%. m.p.134-135°C. Anal. Calcd for $C_{14}H_8N_4O_3$: C, 60.02; H, 2.84; N, 19.99. Found: C, 60.00; H, 2.88; N, 19.99%. IR: 3099, 3056, (ArCH), 2955, 2862, 2243 (CN), 1700 (C=O), 1605, 1558, 1534 (C=C), 1499, 1470, 1264 (O-CH3) 1107, 1024, 835, 732 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.004 (s, 1H, H-C=O), 9.109 (s, 1H, Ar-H), 7.704 (s, 1H, Ar–H), 7.672-7.651 (d, J = 8.4, 1H, Ar-H) 7.542-7.521 (d, J = 8.4, 1H, Ar-H), 3.816 (s, 3H, O-CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 56.72, 113.27; 113.88 (CN), 114.50, 123.64, 124.21, 127.59, 131.16, 136.09, 140.96, 144.67, 151.63, 159.16, 192.39.

5,6-bis(4-Formyl-2-methoxyphenoxy)pyrazine-2,3-dicarbonitrile, 2

5,6-Dichloropyrazine-2,3-dicarbonitrile (0.3 g, 1.5 mmol) and 4-hydroxy-3-methoxybenzaldehyde (0.45 g, 3 mmol) were stirred in 25 mL THF at 65°C. Then triethylamine (0.4 mL, 3 mmol) was added to the mixture stirred at 65°C for 24 h. After the mixture was evaporated to dryness the remaining residue was dissolved in ethanol and then precipitated by addition of water. The light yellow precipitate was collected by filtration. The crude product was purified by crystallisation from dry amyl alcohol.

The yield of light yellow crystals 92%. m.p.196–197°C. Anal. Calcd for $C_{22}H_{14}N_4O_6$: C, 61.40; H, 3.28; N, 13.02. Found: C, 61.41; H, 3.26; N, 13.04%. IR: 3071 (ArCH), 2976, 2944, 2850, 2238 (CN), 1700 (C=O), 1604, 1543 (C=C), 1497, 1437, 1273, 1223 (O-CH_3) 1110, 956, 732 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.023 (s, **2**H, H-C=O), 7.743-7.739 (d, J = 1.6, 2H, Ar-H) 7.701-7.681 (dd, J = 8, 2H, Ar-H), 7.621-7.601 (d, J = 8, 2H, Ar–H), 3.879 (s, 6H, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ 56.84, 113.36, 113.88 (CN), 123.70, 124.17, 124.50, 136.19, 144.71, 150.64, 151.52, 192.41.

General synthesis procedure of zinc(II)azapthalocyanines, 1a and 2a

Compouds **1** and **2** (2 mmol) with zinc acetate (0.5 mmol) were mixed and heated at 250°C for 20 min, respectively. After cooling, the blue products were washed with common solvents (water, ethanol, methanol, ether). The obtained blue-green products were purified using column chromatography ($CHCl_3$-EtOH, 10:1, silica gel).

Zinc(II) azaphthalocyanine, 1a

The yield of green solid 74%. m.p.>300°C. Anal. Calcd for $C_{56}H_{32}N_{16}O_{12}Zn$: C, 56.70; H, 2.72; N, 18.89. Found: C, 56.73; H, 2.74; N, 18.87%. IR: 3064 (ArCH) 2939, 2836, 1685 (C=O), 1597 (C=C), 1532, 1483, 1389, 1316, 1285 (O-CH_3) 1265, 1193, 1146, 1109, 1069, 1025, 983, 731 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.20 (s, 4H, H-C=O), 9.36-9.11 (m, 4H, Ar-H),

Table 4 — Crystal data and structure refinement parameters for compounds **1** and **2**.

Crystal data	**1**	**2**
Empirical formula	$C_{14}H_8N_4O_3$	$C_{22}H_{14}N_4O_6$
Formula weight	280.24	430.37
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	9.9981 (7)	9.8798 (9)
b (Å)	6.6409 (5)	14.9377 (16)
c (Å)	20.2144 (14)	14.0105 (13)
β (º)	98.926 (2)	89.964 (10)
V (Å^3)	1325.91 (16)	2067.7 (3)
Z	4	4
D_c (g cm^{-3})	1.404	1.383
μ (mm^{-1})	0.10	0.10
θ range (º)	3.1-28.3	3.1-24.8
Measured refls.	34730	15052
Independent refls.	3268	3158
R_{int}	0.034	0.074
S	1.11	1.05
R1/wR2	0.058/0.136	0.103/0.349
$\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ^{-3})	0.28/-0.22	0.62/-0.55

8.18-7.53 (m, 12H, Ar–H), 3.99-3.81 (m, 12H, O-CH3). MS: *m/z* 1186.58 [M+1]; UV-Vis (DMSO): λ_{max} nm^{-1} 355, 579, 635.

Zinc(II) azaphthalocyanine, 2a

The yield of blue solid 72%. m.p.>300°C. Anal. Calcd for $C_{88}H_{56}N_{16}O_{24}Zn$: C, 59.15; H, 3.16; N, 12.54. Found: C, 59.16; H, 3.14; N, 12.55%. IR: 3075 (ArCH) 2920, 2850, 1688 (C=O), 1644, 1601 (C=C), 1544, 1498, 1388, 1321, 1269 (O-CH_3) 1220, 1145, 1109, 1025, 920, 732 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 10.02 (s, 8H, H-C=O), 7.73-7.60 (m, 24H, Ar-H), 3.87 (s, 24H, O-CH_3). MS: *m/z* 1787.5 [M+1]; UV-Vis (DMSO): λ_{max} nm^{-1} 338, 575, 631.

X-ray diffraction analysis

Suitable crystals of compunds **1** and **2** were selected for data collection which was performed on a D8-QUEST diffractometer equipped with a graphite-monochromated Mo-K_α radiation at 296 K. The structure of compounds **1** and **2** was solved using SHELXS-97 [11] and refined by full-matrix least-squares methods on F^2, using SHELXL-97 [11], from within the WINGX [1] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. The H atoms of C atoms were located from different maps and then treated as riding atoms with C-H distances of 0.93-0.97 Å. Molecular diagrams of compounds **1** and **2** were created using MERCURY [6]. Supramolecular analyses were made and the diagrams were prepared with the aid of PLATON [13]. Details of data collection and crystal structure determinations are given in Table 4.

α-Glucosidase inhibition assay

α-Glucosidase from *Saccharomyces cerevisiae* (Sigma- Aldrich) inhibition assays were performed spectrophotometrically according to previously published study in the literature[10]. The enzyme solution 20 U/mL was prepared in phosphate buffer (*p*H 6.8, 50 mM). Test compounds were dissolved in 70% methanol. In test tubes, 200 µL of test sample, 5 µL of the enzyme (20 U/mL) and 1245 µL of buffer (*p*H 6.8, 50 mM) were added and incubated for 15 min at 37 ºC. After incubation period, 250 µL of *p*-nitrophenyl-α-D-glucopyranoside (2 mM, Sigma-Aldrich) was added and change in absorbance was monitored for 20 min at 400 nm. Test compound was replaced by methanol (14% final) as control. Acarbose (Sigma-Aldrich) was used as a standard inhibitor. The assays were done in triplicate. The IC_{50} value was determined as the concentration of compound that give 50% inhibition of maximal activity.

Conclusion

The synthesis and characterization of peripheral tetra and octa vanillin substituted novel ZnAzaPcs were accomplished. α-glucosidase enzyme inhibition properties of the novel AzaPcs (**1**, **2**, **1a** and **2a**) were investigated. Consequently, azaphthalonitrile compounds (**1** and **2**) inhibited α-glucosidase to a greater extent than the AzaPcs (**1a** and **2a**) compounds. When compared to acarbose, compound **2** exhibited potent α-glucosidase inhibitory activity in a dose dependent manner.

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1062940 for compound **1**, and 1058247 for compound **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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